

LCS Control Limits

A Modest Proposal



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Proposal

- Use the TNI / NELAC Fields of Proficiency Testing (FoPT) regression equations to establish laboratory control sample (LCS) control limits



EPA Region 8

- 6 states
- 27 Tribal Nations
- 15 National Parks



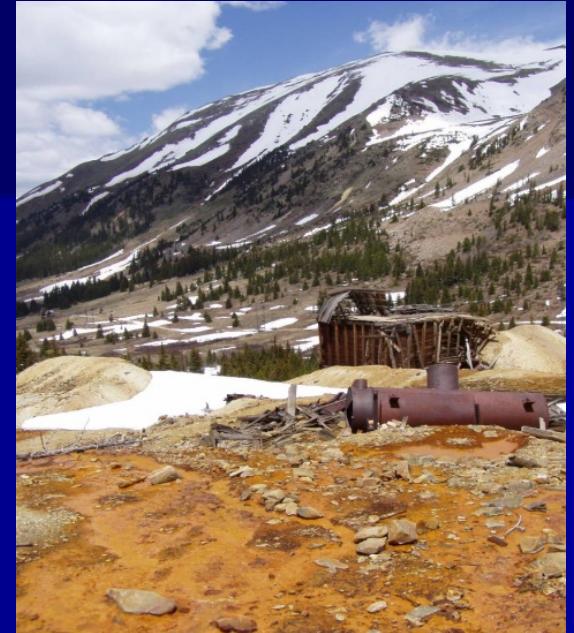
Region 8 Laboratory

- Full service laboratory
- NELAP accredited
 - Drinking water
 - Non-potable water
- Field sampling support
- Certifying Officers for drinking water
- PSL for Wyoming



Analytical Areas

- Metals
 - ICP-OES
 - ICP-MS
- Wet chemistry
 - Anions
 - Alkalinity
- GC
 - GRO / BTEX
 - DRO
 - EDB / DBCP
- GC/MS
 - VOCs
 - SVOCs
- HPLC
 - Pesticides
 - PPCPs
- Microbiology



LCS Control Limits - Sources

- DoD LCS Study
- Method requirements
- TNI / NELAC FoPT regression equations?



DoD LCS Study

- Published 2004
- Focused on nine SW 846 methods
- Based on empirical data
 - Performed in cooperation with ACIL
 - Over 20 participating laboratories
 - Doing work for DoD
 - Considered to be “good performing”
- Used to establish benchmarks for DoD
 - PT regression equations considered a “benchmark”
 - PT limits generally less stringent than LCS Study limits



PT Regression Equations

- Three matrices
 - Drinking water
 - Non-potable water
 - Solid and chemical materials
- Based on empirical data
- Acceptance criteria
 - Mean recovery: $a * \text{conc} + b$
 - Standard deviation: $c * \text{conc} + d$
- Reviewed and updated periodically
 - TNI SOP 4-101



Comparison to LCS Study as Benchmark

LCS Study

- Nine methods
 - Water
 - Solids
- Unique analyses
 - Explosives
 - 2 Aroclors
- No concentration dependence

PT Equations

- Twelve⁺ methods
 - Water
 - Solids – limited
 - Drinking water - limited
- Unique analyses
 - GRO
 - DRO
 - Anions
 - 7 Aroclors, including PCBs in oil
 - Miscellaneous analytes
- Concentration dependant



Ground Rules for Comparing acceptance criteria with LCS Study

- Use non-potable water equations
- Use a mid-range concentration
- Focus on overall properties of analytical groups



Comparison to LCS Study as Benchmark – Metals in Water

LCS Study

- Mean recovery
 - 24 analytes (including Hg)
 - 98.7%
- Standard deviation
 - 4.2%

PT Equations

- Mean recovery
 - 28 analytes (including Hg)
 - 99.7%
 - $a(\text{ave})$: 0.998
- Standard deviation
 - 5.1%
 - $c(\text{ave})$: 0.050

Method 200.7: $\pm 15\%$
Method 200.8: $\pm 15\%$



Comparison to LCS Study as Benchmark – Volatiles in Water

LCS Study

- Mean recovery
 - 69 analytes (including surr)
 - 98.5%
- Standard deviation
 - 10.9%

PT Equations

- Mean recovery
 - 33 analytes
 - 98.4%
 - $a(\text{ave})$: 0.982
- Standard deviation
 - 12.0%
 - $c(\text{ave})$: 0.113



Comparison to LCS Study as Benchmark – Semivolatiles in Water

LCS Study

- Mean recovery
 - 69 analytes (including surr)
 - 77.7%
- Standard deviation
 - 12.1%

PT Equations

- Mean recovery
 - 62 analytes
 - 77.3%
 - $a(\text{ave})$: 0.759
- Standard deviation
 - 17.9%
 - $c(\text{ave})$: 0.168



Extension to Other Analyses

Anions

- 7 analytes
- Mean recovery: 99.8%
 - $a(\text{ave})$: 0.998
- Standard deviation: 5.9%
 - $c(\text{ave})$: 0.048
- Method 300.0: $\pm 10\%$
- R8L:
 - Mean recovery: 97.6%
 - Standard deviation: 4.6%



Extension to Other Analyses

Gas Range Organics

- Analyte: GRO
- Mean recovery: 106.1%
- a: 1.068
- Standard deviation: 25.1%
- c: 0.216
- R8L (MS detection):
 - Mean recovery: 95.5%
 - Standard deviation: 7.0%
 - Use \pm 30% for BTEX compounds



Extension to Other Analyses

Diesel Range Organics

- Analyte: DRO
- Mean recovery: 73.1%
- a: 0.779
- Standard deviation: 19.3%
- c: 0.136
- R8L LCS:
 - Mean recovery: 86.6%
 - Standard deviation: 12.3%



Extension to Other Analyses

PCBs in Water

- 7 Aroclors
- Mean recovery: 88.6%
- $a(\text{ave})$: 0.878
- Standard deviation: 18.0%
- $c(\text{ave})$: 0.192



Conclusions

- LCS Study and PT regression equations lead to similar results
 - Especially true for mean recoveries
 - Use ± 2 SD for in-house limits?
- When the analytical process includes extraction, the mean recoveries will be less than 100%
- The a term is most important in determining the %R
- Both the c and d terms are important in determining the standard deviation
 - Increasingly true as concentration decreases



Advantages of Using PT Regression Equations

- Provide a benchmark for analyses not in the LCS Study
 - Examples: DRO analysis, PCBs in oil
 - Use in absence of in-house statistical limits
- Control limits are concentration dependant
 - Slight
- Have regular review with periodic updates
 - Get DoD out of the business of maintaining



Questions?

